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HYDRIDES AND BOROHYDRIDES OF
LIGHT WEIGHT ELEMENTS AND
RELATED COMPOUNDS

Technical Report
for the period August 1, 1952 to July 31, 1953
for
T. O. Ten, Contract W6ori-20
Project NR 356-255

by
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in cooperation with
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The University of Chicago
August 1, 1953

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INTRODUCTION AND ABSTRACT

During the early part of the contract year just closed, a number of breaks occurred in our vacuum lines, one of which led to an explosion but none of which caused injury to personnel. Realizing that these accidents were probably largely due to the age of the vacuum lines, parts of which had been in use for a long time, we have devoted considerable time to rebuilding all of them completely. As a result the laboratories are now in excellent condition. Additional time had to be devoted to training of replacements for Dr. Riley Schaeffer and for Mr. Amos Leffler who resigned as of August 1 and October 1 respectively.

The work covered by this report is to a considerable extent a continuation of work previously begun or planned. The investigation of the solubility of diborane in ethyl ether at temperatures between 0° and 25° C. and at pressures between 100 mm. and 500 mm. has been completed. The fact that the solubility of the diborane is not proportional to its partial pressure is interpreted as due to partial formation of a borine etherate. This assumption leads to equations which fit the data very satisfactorily. Within the temperature and pressure ranges mentioned, the reaction between lithium borohydride and borofluoride seems to be irreversible in ether solution. It is intended, as soon as adequate personnel is available, to extend these measurements to wider pressure and temperature ranges.

Although progress in the study of the sub-chlorides of boron is necessarily slow because of the time required to produce even very small quantities of the desired compounds, considerable advances have been made. The decomposition of the di-diethyl etherate of B_2Cl_4 into the mono-etherate, and the decomposition of the latter into ethyl chloride and as yet unidentified products has been studied. One mole of tetrachlorodiborine, B_2Cl_4 , in ether solution has been shown to take up one mole of diborane to form a relatively unstable product. The addition of one mole of tetrachlorodiborine to one mole of ethylene, in the absence of any solvent, leads to a more stable product. Further study of the products of these reactions should lead to results of considerable theoretical interest. The tetrachloride also reacts with lithium hydride in the presence of diethyl ether; whether the ether soluble solid product is lithium borohydride or some new type of hydride has not yet been ascertained. The reaction of the sub-chloride B_2Cl_4 with dimethyl zinc seems to result in the formation of a monomethyl derivative. Its reaction with water and with methanol has led to conclusions concerning its structure as is described in the major portion of this report.

Two new solid hydrazine-borine derivatives, $N_2H_4 \cdot 2B(CH_3)_3$ and $N_2H_4 \cdot B_2H_2(CH_3)_4$, have been prepared. The former undergoes reversible dissociation at about 0° C. At temperatures below 200° C. mixtures of hydrazine and a large excess of trimethyl boron (used to decrease dissociation of the adduct) undergo no appreciable chemical change; at higher temperatures methane is formed and the nitrogen to nitrogen bond is broken, as shown by the formation of B-dimethylaminoborane as the only major product. The tetramethyldiborane adduct, which melts at about 10° C., slowly loses two moles of hydrogen per mole of adduct at room temperature. The product is a liquid of a molecular weight (by vapor density) corresponding closely to the formula $R_2B \cdot NH \cdot NH \cdot BR_2$. From the liquid a solid is slowly deposited. Whether this is a polymer of the liquid can probably be ascertained by molecular weight determinations, since the solid is soluble in benzene from which it can be recrystallized. It seems relatively inert toward air and moisture. These new hydrazine derivatives are compared with those previously reported.

As an approach to a detailed study of borazole derivatives, the preparation of B-chloro, B-methyl borazoles has been investigated. Since the use of ethers was considered undesirable, Grignard reagents were avoided, and attention was directed toward metal alkyls. Considerable time was devoted to efforts to ascertain temperatures at which trimethyl boron or dimethyl zinc might partially methylate trichloroborazole without causing decomposition of the latter. No satisfactory results were obtained. Indications are that dimethyl zinc used in toluene at about 50° C. may lead to the desired result.

Experiments have been started on the pyrolysis of methyldiboranes, i.e., of mixtures of diborane with large excesses of trimethyl boron. The reactions are very complex and the identification of the products is difficult. Although the work is in its earliest stages a few tentative conclusions may be drawn from the qualitative observations thus far made, as is described in the body of the report, where a few other brief experiments are mentioned.

A considerable number of papers by the director of the project and his numerous collaborators has been published during the current contract year. Those involving work done under Navy auspices have been distributed as technical reports. They are listed in the main body of this report. Mr. Amos Leffler has presented to the department of chemistry at the University of Chicago a thesis based on his work on the solubility of diborane in ether and on the reversibility of the reaction between lithium borohydride and borofluoride.

I. THE SOLUBILITY OF DIBORANE IN ETHYL ETHER AND THE REACTION BETWEEN LITHIUM BOROHYDRIDE AND BOROFUORIDE.

A. The Solubility of Diborane in Ethyl Ether.

As was pointed out in previous reports (F.R. '51 and '52)¹ fairly accurate data about the solubility of diborane in diethyl ether at several pressures and temperatures are required to determine quantitatively whether the reaction



is reversible in this solvent. If the solution obeys Henry's law the fraction

$$F = \frac{C}{P} \tag{2}$$

in which C is the number of mmoles of diborane taken up per 100 g. of liquid ether and P is the partial diborane pressure in millimeters, should be a constant. Early experiments carried out in the pressure range of about 100 - 500 mm. and at temperatures from 0° C. to 25° C. indicated that the values of F were probably not constant, but decreased slightly with increasing pressures. More reliable experiments completed about September 15, 1952, but not hitherto reported now fully confirm this observation as shown in Tables I and II.

Table I
Solubility of Diborane in Diethyl Ether at 0° C.

| Expt. No. | F ₁ | P ₁ | F ₂ | P ₂ | F ₃ | P ₃ | F ₄ | P ₄ |
|--------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| XLI | 0.0955 | 505 | 0.0956 | 445 | 0.0948 | 394 | - | - |
| XXXIX | 0.0964 | 454 | 0.0957 | 401 | 0.0963 | 350 | 0.0959 | 308 |
| XXVI | 0.0978 | 441 | 0.0995 | 389 | - | - | - | - |
| XLVI | 0.0990 | 315 | 0.0975 | 280 | 0.0985 | 246 | 0.0995 | 216 |
| XXV | 0.1026 | 233 | 0.1039 | 206 | 0.1048 | 182 | - | - |
| XXIII ^a | 0.1050 | 182 | 0.1085 | 145 | 0.1118 | 127 | - | - |

^a The measurements on which the data in this horizontal row are based were preceded by a number of withdrawals made at higher temperatures. The data here recorded are, therefore, probably less reliable than those for the other experiments, since the data become less reliable with each successive withdrawal.

¹ The symbol F.R. stands for Final Report for the year ending on June 30th or July 31st of the year indicated by the numerals.

Table II
Solubility Data at 9.3° C.

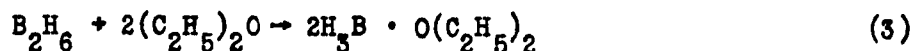
| | | | | | | | |
|-----|--------|--------|--------|--------|--------|--------|--------|
| F | 0.0829 | 0.0837 | 0.0844 | 0.0847 | 0.0852 | 0.0857 | 0.0867 |
| Pmm | 269 | 238 | 213.4 | 213 | 196 | 190.6 | 189 |

In order to clarify the tables it is necessary to review briefly the method used to determine the values of C and P, as described more fully in F.R. '51, pp. 4-5. Known amounts of diborane and of ether were introduced into a reaction vessel which was connected to a "sampling bulb" and a circulating pump. After the mixture had reached the desired temperature the vapors were circulated through the apparatus in such a way as to bubble them through the solution and thus to assure attainment of equilibrium. After a suitable stirring period, the sampling bulb was isolated from the rest of the apparatus and the contents of the former were removed to a vacuum line for analysis. From the results of the analysis the partial pressure of the diborane and its quantity in the vapor phase could be calculated, as is described in detail later. Subtraction of the latter amount from the initial total diborane then gave the amount of diborane in solution.

The first removal of vapor from the sampling bulb and its analysis gives the values designated by the subscript 1 attached to the symbols F and P in Table I. After the first removal, the sampling bulb was reopened to the rest of the apparatus, equilibrium was re-established, the sampling bulb was again isolated and its contents again analyzed. The data from such a second and subsequent withdrawals are indicated by the subscripts 2, 3 and 4. In Table II the F values for the pressure 213.4 and 190.6 mm were successive values in experiment XXIX and the remaining values were taken from experiment XXVIII.

The trend referred to is particularly noticeable in the values of Table II and in the F_1 values of Table I as well as in the F_1 , F_2 , and F_3 values for experiments XLVI, XXV and XXIII. It is not evident in the F_2^3 and F_3 values of the first two experiments of Table I. Since these values correspond to the highest pressures, it appears that the trend is the more pronounced at the smaller pressures. This conclusion is supported by the fact that two solubility determinations made at 24.65° C. led to the F values 0.0748 and 0.0766 for the pressures 115.2 and 99.0 respectively.

It was pointed out in F.R. '52, pp. 15 to 16, that such a trend could be accounted for on the assumption that, at the pressures and temperatures in question, diborane reacts reversibly but incompletely with diethyl ether according to the equation:



It was then shown that under these conditions F should be represented by the equation:

$$F = \frac{\text{C}_{\text{B}_2\text{H}_6} + \frac{1}{2}\text{C}_{\text{H}_3\text{B} \cdot \text{OEt}_2}}{P} \quad (4)$$

in which the symbols C represent, for each of the substances indicated by the subscripts, the number of mmoles per 100 g. of solvent ether. According to Henry's law the term $C_{B_2H_6}$ should be equal to the product $K_H \cdot P_{B_2H_6}$ in which K_H is the Henry law constant, whereas the term $C_{H_3B \cdot OEt_2}$ should be equal to the product $(K_E \cdot C_{B_2H_6})^{\frac{1}{2}}$ in which K_E is the equilibrium law constant for the formation of the borine etherate. Substitution of this value in equation (4) leads to equation (5):

$$F = K_H + \frac{K'}{P^{\frac{1}{2}}} \quad (5)$$

In equation (5) $K' = (K_E K_H)^{\frac{1}{2}}$.

As is to be expected from equation (5) plots of the values of F of Tables I and II against the corresponding values of $1/P^{\frac{1}{2}}$ prove to be straight lines (Figure 1), which conform to the equations:

$$F_{0^\circ C.} = 0.0802 + \frac{0.339}{P^{\frac{1}{2}}} \quad (6)$$

and

$$F_{9.3^\circ C.} = 0.0687 + \frac{0.232}{P^{\frac{1}{2}}} \quad (7)$$

How closely these equations reproduce the experimentally observed values of F (i.e., values of F obtained by dividing by P the total amount of diborane taken up by 100 g. of ether) is shown in Tables III and IV.

Table III

Calculated and Observed F Values at 0° C.

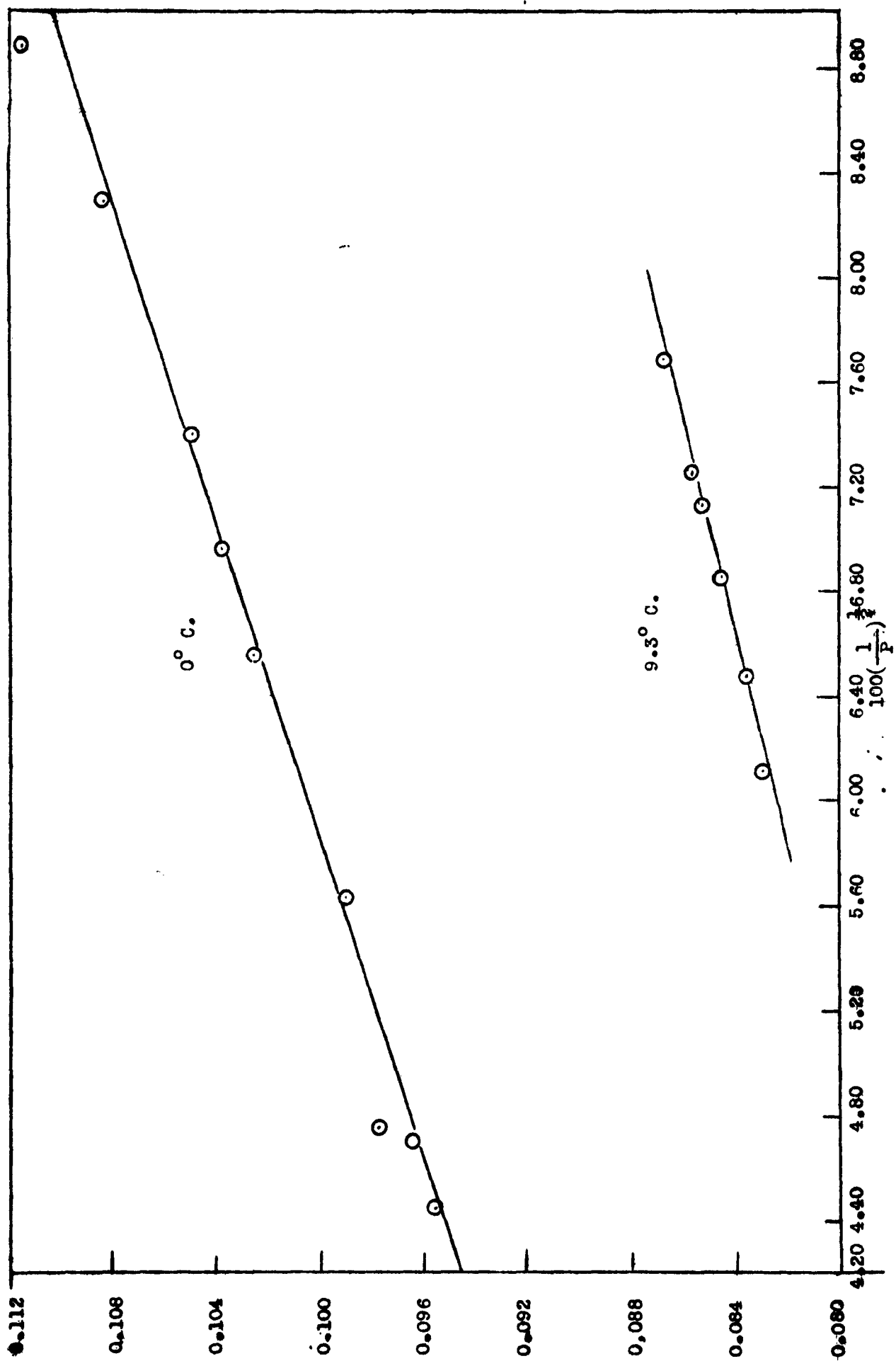
| | | | | | | | | | |
|------------------------|------|------|--------|------|-------|-------|-------|-------|---------|
| P | 505 | 454 | 441 | 315 | .233 | 0.206 | 0.182 | 145 | 127 |
| $F \times 10^2$ (calc) | 9.53 | 9.61 | 9.63 | 9.93 | 10.24 | 10.38 | 10.53 | 10.84 | 11.03 |
| $F \times 10^2$ (obsv) | 9.55 | 9.64 | (9.78) | 9.90 | 10.24 | 10.39 | 10.50 | 10.85 | (11.18) |

Table IV

Calculated and Observed F Values at 9.3° C.

| | | | | | | |
|------------------------|------|------|-------|------|-------|------|
| P | 268 | 238 | 213.4 | 196 | 190.6 | 169 |
| $F \times 10^2$ (calc) | 8.29 | 8.37 | 8.44 | 8.53 | 8.55 | 8.66 |
| $F \times 10^2$ (obsv) | 8.29 | 8.37 | 8.47 | 8.52 | 8.57 | 8.67 |

FIGURE ONE



It will be noted that, aside from the F_2 and F_3 values of experiments XLI and XXXIX (Table I) which were omitted for reasons already mentioned, all but two of the calculated values agree within experimental error with those observed.

From the two values of F and P cited above as obtained at 24.65°C ., K_H and K' at this temperature have the values recorded in equation (8):

$$F_{24.6^\circ\text{C.}} = 0.0558 + \frac{0.205}{P^{\frac{1}{2}}} \quad (8)$$

Although the value of K_H at 24.65°C ., i.e., 0.0558, is based on only two sets of experimental data and is, therefore, less reliable than the values for 0° and 9.3°C ., it has nevertheless been combined with the later two values to derive equation (9):

$$\log K_H = -3.025 + \frac{526.6}{T} \quad (9)$$

As shown in Table V this equation reproduces the three K_H values fairly well. From it one may derive the value -2400 cal/mole for the heat of solution of diborane in ether.

Table V
Calculated and Observed Values of K_H at Three Temperatures

| $t^\circ\text{C.}$ | 0° | 9.3° | 24.6° |
|----------------------------|-----------|-------------|--------------|
| K_H (calc) $\times 10^2$ | 8.00 | 6.92 | 5.55 |
| K_H (obsv) $\times 10^2$ | 8.02 | 6.84 | 5.58 |

Our results depart considerably from those of Elliott, Roth, Roedel and Boldebeck (J.A.C.S., 74, 5211 (1952)). At 20° , for example, they report for the quotient of the diborane concentration by the diborane pressure the values 0.064, 0.053, and 0.056 at pressures of 1687, 2447 and 3526 mm. respectively.² These values do not show the trend demanded by equations of the type $F = A + \frac{B}{P^{\frac{1}{2}}}$, nor do they agree with the values

0.064, 0.063 and 0.062 calculated by us from such an equation.³ At lower temperatures the divergences are even greater. Although the procedure used by them is admittedly not of the highest degree of precision, we hesitate to ascribe the differences ~~in~~ the results of the two investigations entirely to inaccuracies of the earlier one. It seems more likely that the discrepancies are due to what is essentially too extreme an extrapolation, since the constants used in our equations are derived from measurements at pressures between about 100 to 500 mm., whereas their data lie in the pressure range

² The values given here are expressed in the units used by us.

³ In the calculation we used for A the value 0.0592, obtained from equation (9) and estimated the value 0.210 for B .

from about 1100 to 5000 mm. At the higher pressures, the mixtures of diborane and ether vapor may no longer obey the perfect gas laws or Dalton's law; as is the case in the pressure range employed by us. (The validity of the gas laws at the pressures employed by us has been shown by the work of S.H. Smith, Jr., and R.R. Miller, J.A.C.S., 72, 1452 (1950). The validity of Dalton's law is discussed in F.R. '52, p. 14.) It is interesting that, in spite of the disagreement in the two sets of solubility values, the heat of solution calculated by Elliott et al. is 2000 cal. as compared with our value of 2400 cal. per mole.

From the constants of equations (6), (7), and (8), it is possible by the formula $K' = (K_H K_E)^{\frac{1}{2}}$ (as in equation (5)), to calculate values for

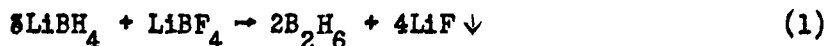
the equilibrium constant, K_E , for the reaction $B_2H_6 + 2(C_2H_5)_2O \rightleftharpoons 2H_3B \cdot O(C_2H_5)_2$. The values so obtained are 1.43, 0.78 and 0.75 for K_E at 0° , 9.3° and 24.6° respectively. We consider the reliability of these values to be rather low, especially in the case of the last one since the calculation of the constants for equation (8) was based on only two values each for F and P. For this reason we consider it unjustified to make a calculation of the heat of reaction.

Although there is considerable evidence supporting the hypothesis that when diborane dissolves in diethyl ether a part of the former is converted to a borine-diethyletherate, we do not consider the hypothesis fully corroborated. There are needed additional data covering larger pressure and temperature ranges and additional determinations to supplement the two carried out at about 25° C. For the purpose, however, of determining whether the reaction between lithium borohydride and borofluoride is reversible, equations of the type $F = K_H + \frac{K'}{P^{\frac{1}{2}}}$ may be satisfactorily used, whether they are well

grounded in theory or whether they are to be considered merely empirical statements of fact.

B. The Reaction Between Lithium Borohydride and Borofluoride.

The procedure for determining whether the reaction



goes to completion, or if it should not, what the equilibrium constant might be, was essentially the same as that for the solubility determinations. That is, known quantities of solid lithium borohydride, solid lithium borofluoride, gaseous diborane and liquid diethyl ether were introduced into the reaction vessel, which was then opened to the sampling bulb. After the reaction vessel had attained the desired temperature and the circulating pump had been in operation long enough to assure equilibrium,⁴ the contents of the sampling bulb were removed for analysis.

From the results of the analysis and from the known volumes of the sampling bulb and of the total free gas space of the entire apparatus, the partial diborane pressure and the total quantity of gaseous diborane

⁴ At 0° C. equilibrium was established very slowly. A number of orienting experiments had first to be carried out to ascertain the minimum time required for completion of the reaction.

present were calculated, as in the solubility determinations. The amount of diborane which had gone into solution was then calculated from the pressure by the equations:

$$F = K_H + \frac{K'}{P_H} \quad (5)$$

and

$$C = FP \quad (2)$$

in which C is the number of millimoles of diborane taken up by 100 g. of ether. Since the reaction vessel invariably contained less than this quantity of ether the quantity C had to be multiplied by the fraction: wt. ether/100 to obtain the amount of diborane actually dissolved.⁵

In these experiments appreciable quantities of hydrogen were evolved, probably because it was impossible completely to avoid introduction of moisture during the transfer of the solids to the reaction vessel. The hydrogen so evolved constitutes a loss of diborane. Consequently the total diborane obtained is considered the sum of that present in the gas phase plus that gone into solution plus the diborane equivalent of the hydrogen generated. The total amount of diborane calculated as described was then compared with the sum of the amount of diborane originally introduced into the reaction vessel plus that obtainable by complete interaction according to equation(1).

The results are recorded in Table VI. In column 1, the letters A and B attached to the experiment number indicate the results of the first and second withdrawals of diborane from the sampling bulb. In the third and fourth columns, the asterisks indicate which of the two salts was present in less than the stoichiometric ratio. Columns 5 and 6 record the amounts of diborane and of ether initially introduced into the reaction vessel. Column 7 gives the sum of the amount of diborane found to be present in the gas phase, plus that present in the ether solution plus a correction for the amount lost by the action of unavoidable moisture, as described later. Column 8 contains the sum of the amount of diborane originally introduced into the reaction system plus that which would have been formed by complete interaction of the two salts. The latter quantity is twice the initial amount of the borofluoride when the borohydride is present in excess, or 2/3 of the initial borohydride if the other salt is present in excess. The amounts of the salts was so chosen that, if the reaction went to completion or nearly so, the concentration of residual salt would be too small to affect the solubility of diborane.⁶ If two withdrawals were made from the sampling bulb, the theoretically obtainable diborane for the second withdrawal is that calculated for the first withdrawal diminished by the amount that was removed from the sampling bulb in the first withdrawal.

Table VI discloses what, in view of the sources of error, are relatively small differences between the amount of diborane accounted for and that calculated on the assumption of complete reaction. It is true that in

⁵ By the "amount dissolved" is meant the quantity of diborane present as such and that present as $H_3B \cdot O(Et)_2$. The constants K_H and K' were taken from equations (6) and (7) respectively.

⁶ Actual solubility determinations of diborane in ether containing small quantities of the salts justified this assumption.

Table VI
Tabulated Data for Reaction of LiBH_4 with LiBF_4

| Exp. No. | $t^\circ\text{C.}$ | Starting Materials (m.moles) | | | | Total B_2H_6 at equilibrium (m.moles) | Total B_2H_6 Theory (m.moles) | Diff- erence |
|-------------|--------------------|------------------------------|-----------------|------------------------|-------------------------------|--|--|-----------------|
| | | LiBH_4 | LiBF_4 | B_2H_6 | Et_2O (g.) | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| XXXI | 9.3 | 29.67* | 10.78 | 0.00 | 57.47 | 18.90 | 19.78 | -4.4% |
| XXXIII | | | | | | | | |
| A | 9.3 | 7.01 | 2.10* | 17.80 | 29.58 | 21.77 | 22.00 | -1.1% |
| B | 9.3 | 7.01 | 2.10* | 17.80 | 29.58 | 19.06 | 18.95 | +0.5% |
| XLIV | 0.0 | 38.01 | 10.18* | 9.32 | 29.51 | 29.00 | 29.68 | -1.3% |
| XLV | | | | | | | | |
| A | 0.0 | 25.55* | 9.55 | 14.453 | 35.25 | 31.82 | 31.56 | +0.9% |
| B | 0.0 | 25.55* | 9.55 | 14.453 | 35.25 | 27.19 | 27.85 | -2.0% |

* Stoichiometrically deficient compound.

in all but one case the amount of diborane found is slightly less than the calculated value. There are adequate reasons for believing that the discrepancy is not due to incompleteness of the reaction. The closest agreement between observation and theory was achieved in the reaction in which the largest amount of diborane was initially present; under these conditions reversibility would have led to the largest rather than the smallest difference between the observed and calculated values. In the second place the fact that the amount of diborane recovered is usually slightly less than the theory is just what one would expect from the sensitivity of lithium borohydride to air and moisture; it is, therefore, subject to deterioration during the process of transfer from the weighing bottles to the reaction vessel.⁷

It was originally intended to examine the reverse reaction also, i.e., the reaction between lithium fluoride and diborane in the presence of ether. Preliminary experiments showed that such an undertaking would be indecisive. These experiments were carried out in a piece of apparatus consisting of two bulbs joined by glass tubing bent almost at right angles. The tubing carried a sealed-in fritted disk. Into one of the bulbs diborane, lithium fluoride⁸ and ether were introduced under as nearly anhydrous conditions as possible. The apparatus, after it had been sealed, was shaken with care that none of the liquid encountered the disk. After long continued agitation, the apparatus was tilted so that the liquid could be filtered through the disk into the empty bulb which was cooled to facilitate the filtration. The apparatus was then opened to the vacuum line, and the ether was removed. The filtered solution left no, or practically no solid residue as would have been the case if the fluoride had reacted with the diborane.

These results establish that at the temperatures and pressures employed by us the reaction in question is not appreciably reversible. Furthermore in the experiments on the possible reaction of diborane on lithium fluoride the calculated diborane pressures were somewhat greater than atmospheric but also indicated irreversibility. Nevertheless it is possible that at still higher pressures slight reversibility might be observed -- a question which requires further study.

C. Experimental Details.

The apparatus and procedures employed in the solubility and equilibrium studies were described in earlier reports in only schematic fashion. A more detailed description is now given in parts 1 and 2 of this section of the present report. The values of the fractions F and of the partial diborane pressure in Tables I and II are values calculated from the experimental data recorded in Tables VII, VIII, and IX of part 3 of this section. The method of calculation is illustrated in part 4, and the experimental data for the equilibrium experiments are recorded in Table X, part 5.

⁷ The initial quantities of the two salts have been corrected for the presence of impurities. In the case of the borohydride, slight deterioration could headily have occurred after the analysis had been made.

⁸ Several samples of lithium fluoride were used. One of these was obtained by interaction of lithium borohydride and borofluoride in ether. Excess soluble salts were washed away with ether, and the lithium fluoride was used without complete evaporation of the ether, in order to avoid decreasing its reactivity. All samples used, whether prepared in this or other ways, behaved alike.

1.) Apparatus.

The apparatus consisted of a vacuum line such as those described in Stock's and in Sanderson's books⁹, connected to a part in which the solubility and equilibrium experiments were carried out. The vacuum line was used for the preparation and purification of the diborane, for determination of the quantity of diborane initially used in each experiment, and for analysis of the vapor after equilibrium in the two types of experiments had been attained.

The apparatus in which the experiments were carried out consisted, as already mentioned, of a reaction vessel "RV," a "sampling bulb," "SB," and the circulating pump, connected with each other as shown in figure 2. The sampling bulb could be isolated from the rest of the apparatus by means of the one and the two-way stopcocks shown. By appropriate adjustment of the latter, the "equilibrium apparatus" could be opened to the vacuum line or closed off from it. The total volume of the apparatus, as well as the volume of the portion between the two stop-cocks were accurately determined.

The circulating pump and the associated valves E and F, used to assure equilibrium within the solutions and between liquid and vapor, followed a design employed at the Naval Research Laboratory. Instead of the glass piston used there, we employed one made of a thin shell of stainless steel, provided as shown in figure 2, with phosphor bronze springs to take up the impact due to the stroke. Like the glass pistons of the original design, the stainless steel piston contained an iron core. The advantage of the modification used by us is that it avoided breakage resulting from too rapid a piston stroke.

The device which alternately actuated and deactivated the magnets controlling the piston and the valves, and which synchronized the action of piston and valves is shown in figure 3. It consisted of a synchronous motor geared to operate a cam at about 4 R.P.M. An arm controlled by the cam alternately opened and closed a microswitch to energize the solenoids. The pumping cycle consisted of two steps; in the first step the piston and valve E were energized to compress the gas; in the second step, valve F was opened to equalize the pressure in the system. Because the solenoids had a low ohmic resistance they could only be operated for short periods of time without overheating. Operation of the pump circulated the vapors in such a direction that they bubbled through the liquid contained in the reaction vessel and thus not only aided in attaining equilibrium between vapor and liquid, but also stirred the liquid solution.

For reasons already mentioned, only the reaction vessel (RV) was maintained at a constant temperature lower than that of the rest of the apparatus. For the measurements at 0° C., an ice-water mixture contained in a dewar vessel was used as the thermostat; at higher temperatures, an electrically controlled water bath was used. This control circuit is illustrated in Weissberger.¹⁰

⁹ Stock, A., "Chemistry of Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

Sanderson, R., "Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, New York, N.Y., 1948.

¹⁰ Weissberger, A., "Physical Methods of Organic Chemistry," Interscience Publishers, New York, N.Y., 2nd Edition, 1949, p. 42.

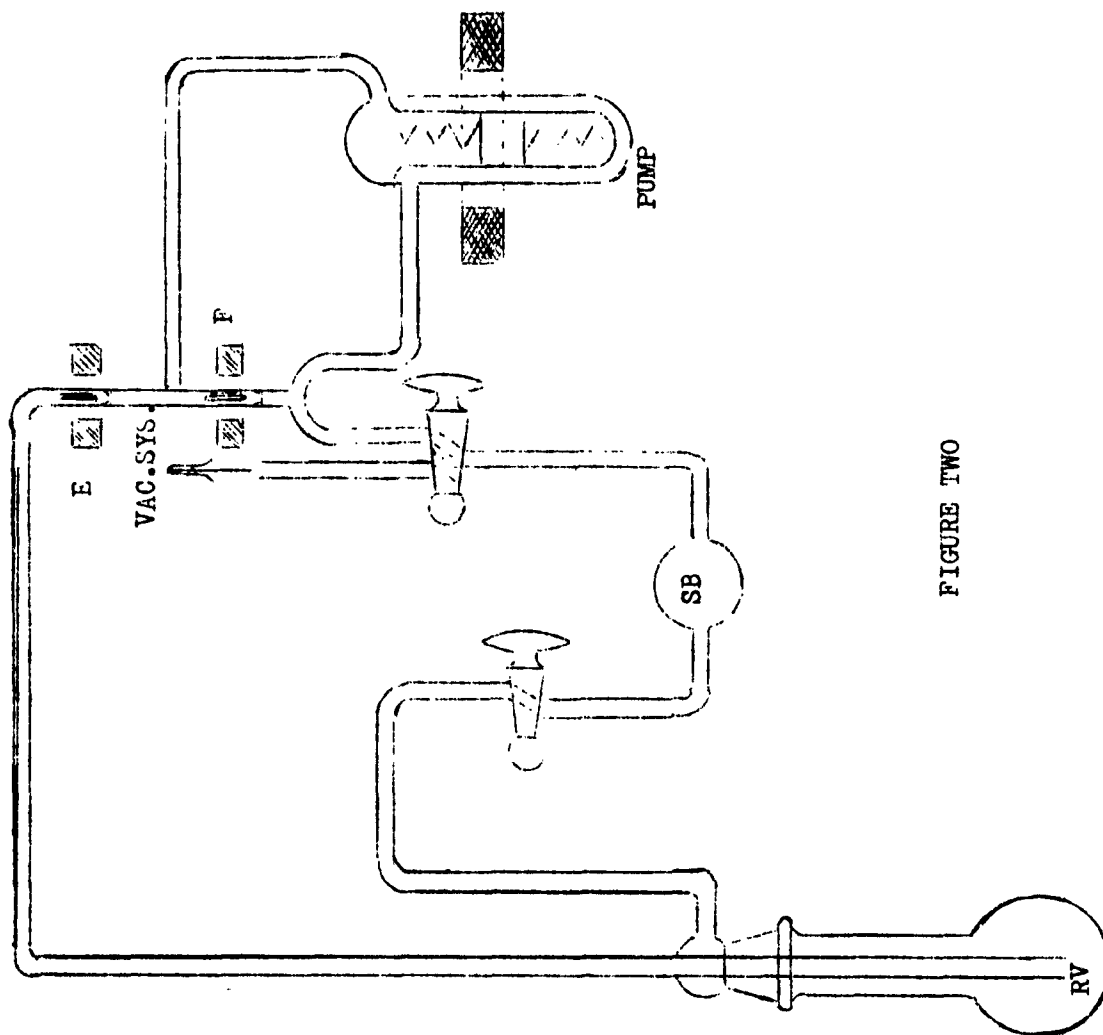
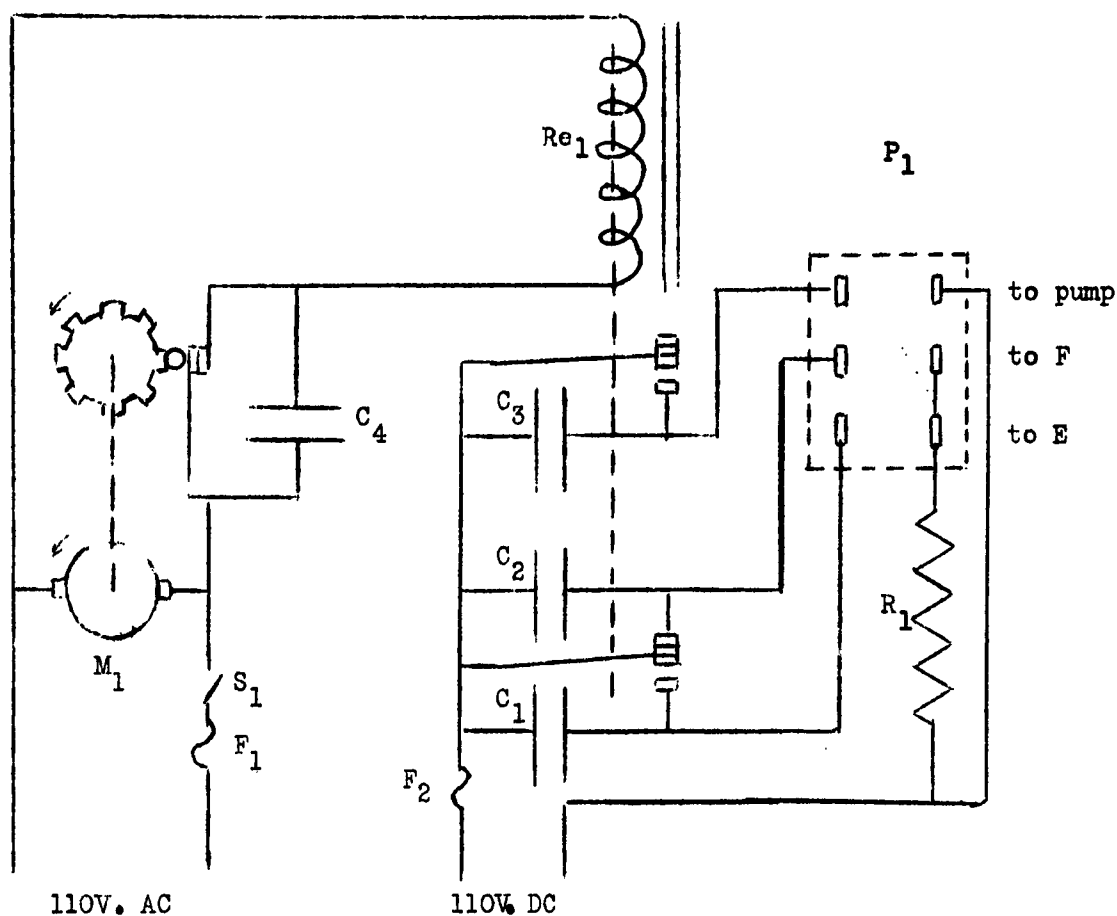


FIGURE TWO



PARTS

| | |
|---|--|
| M ₁ Sync. Motor | F ₁ 5A, 250V. fuse |
| Re ₁ 110V DPDT Relay | F ₂ 3A, 250V. fuse |
| C ₁ , C ₂ .02 MF. | P ₁ Jones Plug |
| C ₃ 2 MF. | R ₁ 400 Ohm, 50 Watt resistor |
| C ₄ 0.1 MF. | |

FIGURE THREE

2.) Procedure.

To determine the solubility of diborane in ether, the following procedure was used. Ether, dried over lithium aluminum hydride, was placed in a flask equipped with a standard taper, weighed, and then attached to the vacuum system. The ether was cooled to liquid nitrogen temperature and the air in the flask pumped out, making certain, by pumping through a trap at liquid nitrogen temperature, that no ether was lost. Then the ether was allowed to warm and a definite amount was distilled into reaction vessel RV (cf. fig. 2). The ether supply flask was then filled with dry nitrogen, removed from the vacuum system and weighed again. The difference between the two weights gave the amount of ether introduced into the equilibrium system.

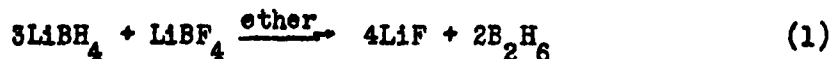
The diborane used was checked for purity by vapor pressure measurement, (225 mm. at -111.9°C.), and measured by the use of a standard volume bulb. It was then condensed into reaction vessel RV by the use of liquid nitrogen. Next the equilibrium system was isolated from the vacuum line by adjustment of the two-way stop-cock, and the ether-diborane mixture was allowed to warm to approximately 0°C.

The ether-diborane mixtures were allowed to stand in the reaction system overnight at the temperature of the experiment, and were then stirred intermittently for three hours. That this procedure assured attainment of equilibrium between diborane and the ether solution had been demonstrated by earlier exploratory experiments. In these, a manometer, attached to the reaction system, showed no changes in the pressure above solutions of diborane in ether after the pump had been operated intermittently for one hour¹¹. After the three hour period of stirring, the sampling bulb was isolated from the rest of the reaction system, and connected to the vacuum line by appropriate adjustment of the stop-cocks. The volatile, but condensable, contents of the sampling bulb were then condensed by use of liquid nitrogen into a suitable portion of the vacuum system. The small amounts of hydrogen usually present in the sampling bulb were removed by a Toepler pump, and measured.

The condensable material was evaporated into a calibrated portion of the vacuum line and its pressure determined at room temperature. This vapor pressure was then used to calculate the vapor pressure of the ether and diborane in the sample bulb. The difference between this calculated vapor pressure and that determined from the hydrolysis of the diborane gave the vapor pressure of the ether at the temperature of the reaction vessel. This always agreed within 5 mm. of the tabulated value or else the determination was rejected. No other use of the vapor pressure was made.

All of the material was then condensed at -196°C. into a 100 ml. side-arm flask which had been connected to the vacuum system by a standard taper, and which contained enough water (frozen) to hydrolyze the diborane. The flask was then sealed off and warmed to room temperature. To complete the hydrolysis, the flask was finally heated on a steam bath. After opening the flask to the vacuum line through a vacuum tube opener, the hydrogen generated was measured in the usual way.

In the experiments for determining whether the reaction:



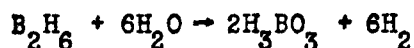
goes to completion, the procedure was essentially the same as that used in

¹¹ The manometer was not retained in the final portion of the apparatus because its inclusion created "dead spaces" which adversely affected the reliability of the results.

the solubility measurements, except that before the introduction of the ether and diborane into the reaction system, the vessel RV was charged with appropriate weighed quantities of dry lithium borohydride and lithium borofluoride. In the experiments involving this reaction at 0° C., the stirring time was considerably lengthened because preliminary experiments indicated that the reaction is fairly slow at that temperature.

3.) Experimental Data for the Solubility Measurements.

The experimental data used in the calculation of the values recorded in Tables I and II and for the solubilities at 24.65° C. (p. 5) are contained in Tables VII, VIII and IX. In the latter tables, column 1 records the weight of liquid ether left in the reaction vessel after the system had become saturated with ether vapor. The method of determining this value not only for the first withdrawal of vapor from the sampling bulb, but also for subsequent withdrawals is described in the "sample solubility calculation." Column 2 represents the uncorrected total amount of diborane present in the system; how this amount is calculated for the experiments indicated by the letters B, C, or D is also described in the "sample solubility calculation." The data of column 3 represent one-sixth of the amount of hydrogen found to be present in the total gas volume at the time of the first withdrawal. This hydrogen is assumed to have resulted from the action of traces of water according to the equation:



It thus constitutes a loss of diborane.¹² Column 4 is obtained by subtracting from the uncorrected total diborane (column 2) the amount lost by this hydrolysis (column 3). (The reason why no such correction is made in experiments labeled B, C, and D is stated in footnote 15, p. 13.) Column 5 records the amounts of diborane vapor found by analysis to have been present in the sampling bulb at equilibrium. Column 6 is the free gas volume of the apparatus. Column 7 records the amounts of diborane in the total gas phase at equilibrium, column 8 the amounts of diborane taken up by the amounts of ether listed in column 1, column 9 the partial diborane pressures, and column 10 the values of the fraction F. The calculations by which the data of columns 6, 7, 8, 9, and 10 are obtained are described in the "sample solubility calculation."

4.) Sample Solubility Calculation.

The steps by which the numerator and the denominator of the fraction

$$F = \frac{\text{mmoles of B}_2\text{H}_6 \text{ per 100 g.}}{\text{partial pressure of B}_2\text{H}_6}$$

¹² Experiments in which this loss corresponded to more than a fraction of one percent were discarded.

Table VII

Experimental Data Used in Calculations of Solubility at 0.0° C.

| Exp. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|----------|---|--|---|---|---|-------------------------------------|--|---|--|--------|
| | Et ₂ O (grams) corrected | B ₂ H ₆ Total (mmoles) | B ₂ H ₆ Lost (mmoles) | B ₂ H ₆ Total corrected (mmoles) | B ₂ H ₆ in sample bulb (mmoles) | Gas Volume corrected (cc.) | B ₂ H ₆ Total in vapor (mmoles) | B ₂ H ₆ Total in solution (mmoles) | P B ₂ H ₆ (mm.) | F |
| XXIII | | | | | | | | | | |
| A | 38.4 | 9.248 | | 9.248 | 0.963 | 413.4 | 3.221 | 6.027 | 144.7 | 0.1085 |
| B | 38.3 | 8.285 | | 8.285 | 0.851 | 413.6 | 2.848 | 5.437 | 127.9 | 0.1110 |
| XXV | | | | | | | | | | |
| A | 36.39 | 13.920 | 0.019 | 13.901 | 1.561 | 416.2 | 5.222 | 8.679 | 233.0 | 0.1026 |
| B | 36.39 | 12.369 | | 12.369 | 1.369 | 416.3 | 4.611 | 7.758 | 205.7 | 0.1039 |
| C | 36.20 | 11.000 | | 11.000 | 1.213 | 416.4 | 4.087 | 6.913 | 182.2 | 0.1048 |
| XXVI | | | | | | | | | | |
| A | 40.20 | 27.148 | 0.017 | 27.131 | 2.943 | 411.0 | 9.786 | 17.345 | 442.2 | 0.0976 |
| B | 40.10 | 24.188 | | 24.188 | 2.598 | 411.1 | 8.634 | 15.551 | 389.9 | 0.0995 |
| XXIX | | | | | | | | | | |
| A | 30.53 | 23.814 | 0.059 | 23.755 | 2.977 | 431.0 | 10.373 | 13.382 | 454.5 | 0.0964 |
| B | 30.42 | 20.778 | | 20.778 | 2.612 | 431.1 | 9.103 | 11.675 | 400.6 | 0.0957 |
| C | 30.35 | 18.166 | | 18.166 | 2.277 | 431.3 | 7.939 | 10.227 | 349.9 | 0.0963 |
| D | 30.26 | 15.889 | | 15.889 | 2.005 | 431.4 | 6.992 | 8.898 | 306.6 | 0.0959 |
| XLI | | | | | | | | | | |
| A | 33.02 | 28.071 | 0.538 | 27.533 | 3.353 | 427.6 | 11.590 | 15.943 | 505.5 | 0.0955 |
| B | 32.93 | 24.180 | | 24.180 | 2.932 | 427.8 | 10.140 | 14.040 | 445.8 | 0.0956 |
| C | 32.84 | 21.248 | | 21.248 | 2.594 | 427.9 | 8.970 | 12.278 | 394.4 | 0.0948 |
| XLVI | | | | | | | | | | |
| A | 33.83 | 17.828 | 0.059 | 17.769 | 2.093 | 426.5 | 7.216 | 10.553 | 314.95 | 0.0990 |
| B | 33.74 | 15.670 | | 15.670 | 1.871 | 426.6 | 6.460 | 9.210 | 280.50 | 0.0975 |
| C | 33.65 | 13.800 | | 13.800 | 1.641 | 426.8 | 5.670 | 8.130 | 246.00 | 0.0985 |
| D | 33.56 | 12.160 | | 12.160 | 1.435 | 426.9 | 4.960 | 7.200 | 216.00 | 0.0995 |

Table VIII
Experimental Data Used in Calculations of Solubility at 9.3° C.

| Exp. No. | 1 Et ₂ O (grams) | 2 B ₂ H ₆ Introduced (mmoles) | 3 B ₂ H ₆ Lost (mmoles) | 4 B ₂ H ₆ Used (mmoles) | 5 B ₂ H ₆ in sample bulb (mmoles) | 6 Gas Volume (cc.) | 7 B ₂ H ₆ Total in gas (mmoles) | 8 B ₂ H ₆ Total in solution (mmoles) | 9 P _{B₂H₆} (mm.) | 10 F |
|---------------|-----------------------------------|--|--|--|--|-----------------------------|---|--|---|---------|
| XXVIII | | | | | | | | | | |
| A | 51.5 | 17.350 | 0.0323 | 17.318 | 1.779 | 416.0 | 5.982 | 11.336 | 267.95 | 0.0825 |
| B | 51.4 | 15.539 | 0.0302 | 15.509 | 1.576 | 416.1 | 5.302 | 10.237 | 237.9 | 0.0837 |
| C | 51.3 | 13.963 | 0.0226 | 13.940 | 1.406 | 416.2 | 4.732 | 9.234 | 212.8 | 0.0847 |
| D | 51.2 | 12.559 | 0.0254 | 12.534 | 1.277 | 416.4 | 4.281 | 8.278 | 189.85 | 0.0852 |
| XXIX | | | | | | | | | | |
| A | 56.5 | 14.834 | 0.073 | 14.745 | 1.417 | 398.1 | 4.564 | 10.181 | 213.4 | 0.0844 |
| B | 56.4 | 13.328 | 0.030 | 13.298 | 1.269 | 398.3 | 4.089 | 9.209 | 190.6 | 0.0857 |

Table IX
Experimental Data Used in Calculations of Solubility at 24.65° C.

| Exp. No. | 1 Et ₂ O (grams) | 2 B ₂ H ₆ Introduced (mmoles) | 3 B ₂ H ₆ Lost | 4 B ₂ H ₆ Used (mmoles) | 5 B ₂ H ₆ in sample bulb (mmoles) | 6 Gas Volume (cc) | 7 B ₂ H ₆ Total in gas (mmoles) | 8 B ₂ H ₆ Total in solution (mmoles) | 9 P B ₂ H ₆ (mm. of hg.) | 10 F |
|-------------|-----------------------------------|--|--|--|--|----------------------------|---|--|---|---------|
| XXIII | | | | | | | | | | |
| A | 37.35 | 5.768 | - | 5.768 | 0.763 | 412.9 | 2.549 | 3.219 | 115.2 | 0.0748 |
| B | 31.10 | 5.005 | | 5.005 | 0.655 | 413.3 | 2.190 | 2.815 | 99.0 | 0.0766 |

were obtained from the data of Tables VII to IX are illustrated by reference first to experiment XXVI A and then to experiment XXVI B of Table VII.

The free gas volume of the apparatus, needed for some of the subsequent steps, was obtained by subtracting the volume of liquid ether from the total volume of the apparatus (465.6 cc.) In experiment XXVI A, 40.51 g. or 55.0 cc. of ether¹³ was introduced into the apparatus, leaving 410.6 cc. for a first approximation of the free volume. This value does not take into consideration the amount of ether that evaporated. But the value 410.6 cc. in conjunction with the known vapor tension and molecular weight of ether could be used to calculate, by the gas laws, the amount of liquid ether lost by evaporation. The calculation in the case of experiment XXVI A led to the value 0.31 g. Hence the corrected value for the weight of ether was 40.51 - 0.31, or 40.20 g. (as recorded in column 1); the corrected volume of liquid ether was 54.6 cc., and the corrected free volume was 465.6 - 54.6 = 411.0 (column 6).¹⁴

The partial pressure of the diborane was calculated according to the gas laws from the amount of diborane (2.943 mmoles, as recorded in column 5), found by analysis to be present in the sampling bulb, in conjunction with the known volume of this bulb (123.6 cc.) and its temperature (297.8° C). The value thus calculated is recorded as 442.2 mm. in column 9.

By multiplying the amount of diborane in the sampling bulb (2.943 mmoles) by the ratio of the total free gas volume to the volume of the sampling bulb, i.e., by 411.0/123.6, the value 9.78 mmoles was obtained for the total amount of diborane in the gas phase (column 7).

To obtain the amount of diborane taken up by the 40.20 g. of liquid ether, the amount of diborane in the gas phase is subtracted from the total amount of diborane present. The latter quantity is the quantity initially measured out (27.148 moles, column 2) less the amount lost by hydrolysis (0.017 mmoles, column 3) or 27.131 mmoles as recorded in column 4. Hence, in experiment XXVI A the amount of diborane in 40.20 g. of liquid ether was 27.131 - 9.786 = 17.345 mmoles (column 8). To obtain the amount of diborane per 100 g. of solvent, the last named quantity was multiplied by 100/40.20 to give 43.147 mmoles. Hence the value of F for the experiment in question was 43.147/442.2 = 0.0976.

The corresponding calculation for experiment XXVI B differs only very slightly from the preceding one. For this case, the total amount of diborane (column 2 for experiment XXVI A) was found by subtracting the amount of diborane removed from the sampling bulb in experiment XXVI A (2.943 mmoles, column 5 for this experiment) from the corrected total amount of diborane of experiment XXVI A, i.e. from 27.131 (column 4), giving the value 24.188 as recorded in column 2 for experiment XXVI B.¹⁵ Since removal of diborane from the sampling bulb in experiment XXVI A carried with it some ether vapor,

¹³ The density of ether at 0° C. is 0.736 g./cc.

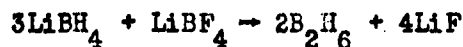
¹⁴ Actually the liquid in the apparatus is a solution of diborane in ether rather than pure ether, and the use of the vapor tension of the latter in the calculation of the ether lost by evaporation introduces an error. However, since the amount of liquid calculated as lost by evaporation never amounted to more than about one per cent and since the mole fraction of diborane in these experiments was relatively small, the error introduced by neglecting the lowering of the ether vapor tension of the ether was insignificant.

¹⁵ No further correction for loss of diborane is needed since only in experiments that were discarded was there evidence of additional hydrogen evolution. Hence the values recorded in columns 2 and 4 for XXVI B are identical.

a correction was made for the amount of liquid so lost. The correction was calculated as was the calculation for the amount of ether lost by evaporation, except that in this case the volume of the sampling bulb instead of that of the whole apparatus was used. In the case in question the amount of ether withdrawn was calculated to be 0.1 g., leaving 40.1 g. (column 1) for the residual ether. In cases in which more than two samples of diborane were removed, the pattern of calculation followed that described for experiment XXVI B.

5.) Experimental Data for the Equilibrium Experiments.

The experimental data which led to the calculation that the reaction



is not appreciably reversible under the conditions of our experiments are recorded in Table X, the first four columns of which are self explanatory. Column 5 records the amounts of diborane added to the reaction mixture initially in all but the first of the experiments listed. The quantities of ether listed in column 6 represent the initial amounts of ether corrected for the quantities lost from the liquid by evaporation, and for the B experiments by withdrawal from the sampling bulb, as described in the "sample solubility calculation." Column 7 records the quantities of diborane found by analysis to have been present in the sampling bulb after equilibrium between the ether solutions of the two salts and the diborane had been established. The equilibrium partial pressures of diborane (column 8) and the amount of diborane in the free gas space at equilibrium (column 9) were obtained as described in the sample calculation already referred to.¹⁶ The amounts of diborane in solution at equilibrium (column 10) were calculated from equations (5) and (2) as described on page 10.¹⁷ Column 11 records the amount of diborane lost by hydrolysis as discussed in the description of Tables VII, VIII and IX. Column 12 is the sum of the data of columns 9, 10 and 11 and thus represents the total diborane recovered.

Column 13 is the theoretical amount of diborane obtainable from the amount of diborane initially added to the reaction mixture plus that which would have been obtained had the reaction between the borohydride and the borofluoride gone to completion, calculated as described on page 10. Had this condition been fulfilled, the values in columns 12 and 13 should have been identical. Only in experiment XXXI is the departure from this identity beyond experimental error. The greater deviation found in the first recorded experiment is probably also ascribable to experimental error since in this experiment, in which no diborane was added to the reaction mixture, one would expect the smallest degree of reversibility.

¹⁶ The latter also describes the method used for calculating the total free gas space required for several of the calculations.

¹⁷ The appropriate values for the constants K_H and K' were taken from equations (6) and (7), page 6.

Table X
The Reaction of LiBH_4 with LiBF_4

| Exp. No. | t°C | Starting Materials (mmoles) | | | | B ₂ H ₆ in sample bulb (mmoles) | P _{B₂H₆} (mm.) | B ₂ H ₆ at equilibrium (mmoles) | | | | B ₂ H ₆ Theory (mm.) | Diff-erence |
|----------|-----|-----------------------------|-------------------|-------------------------------|------------------------|---|---|---|----------|-------|-------|--|-------------|
| | | LiBH ₄ | LiBF ₄ | B ₂ H ₆ | Et ₂ O (g.) | | | gas | solution | lost | total | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 ^a | 14 |
| XXI | 9.3 | 29.67* | 10.78 | 0.00 | 57.47 | 1.77 | 266 | 5.68 | 12.66 | 0.56 | 18.90 | 19.78 | -4.4% |
| XXIII | | | | | | | | | | | | | |
| A | 9.3 | 7.01 | 2.10* | 17.80 | 29.58 | 3.05 | 461 | 10.76 | 10.75 | 0.26 | 21.77 | 22.00 | -1.1% |
| B | 9.3 | 7.01 | 2.10 | 17.80 | 29.58 | 2.64 | 400 | 9.31 | 9.49 | 0.26 | 19.06 | 18.95 | 0.5% |
| XLIV | 0.0 | 38.01 | 10.18* | 9.32 | 29.51 | 3.59 | 541 | 12.51 | 15.71 | 0.78 | 29.00 | 29.68 | -1.3% |
| XLV | | | | | | | | | | | | | |
| A | 0.0 | 25.55* | 9.55 | 14.453 | 35.25 | 3.71 | 556 | 12.79 | 18.88 | 0.153 | 31.82 | 31.56 | 0.9% |
| B | 0.0 | 25.55 | 9.55 | 14.453 | 35.25 | 3.22 | 482 | 11.04 | 16.15 | 0.153 | 27.19 | 27.85 | -2.0% |

* stoichiometrically deficient compound

^a The data in column 13 for the B experiments were obtained by subtracting the value given in column 7 for the corresponding A experiments from the value given in column 13 for the A experiments.

II. FURTHER STUDIES ON THE SUB-CHLORIDES OF BORON.

A. Reactions of Tetrachlorodiborine.

1.) Etherates.

As previously reported (F.R. '48, p. 28), tetrachlorodiborine forms both a di- and a mono- etherate with diethylether. Neither is very stable as is illustrated by the following example:

A mixture of 2.09 mmoles of tetrachlorodiborine in 8.63 mmoles of diethyl ether was prepared at -80° C. in the absence of air and moisture. By stirring and gradually warming the mixture to room temperature, a clear, colorless solution was obtained. Recooling of the latter to -80° C. caused the precipitation of white crystals, from which 4.59 mmoles of ether could be removed by pumping at temperatures not exceeding -45° C. The 4.04 mmoles of ether thus remaining in the crystals constituted an $\text{Et}_2\text{O}/\text{B}_2\text{Cl}_4$ ratio of 1.93/1.00. When the crystals were warmed to -23° C., an additional 2 mmoles of ether was removed, leaving a yellow viscous liquid in which the $\text{Et}_2\text{O}/\text{B}_2\text{Cl}_4$ ratio was 0.97/1.00. Further warming of the liquid to room temperature resulted in the evolution of 4.55 mmoles of ethyl chloride, or 2.18 mmoles of ethyl chloride per mole of the mono-etherate. In view of the complexity of the experiment and the small quantities involved, this result indicates that all of the ethyl groups in the monoetherate are converted to ethyl chloride, a point of some interest in connection with the behavior of tetrachlorodiborine toward diborane (Section II A (3)) and with the methanolysis of the compound B_2Cl_4 (Section II B (2)). The glassy, yellow solid obtained simultaneously with the ethyl chloride has not yet been studied in detail.

2.) The Reaction of Tetrachlorodiborine with Lithium Hydride.

Although unsolvated liquid tetrachlorodiborine does not react with lithium hydride, a reaction seemed to occur when a mixture containing 2 moles of lithium hydride per mole of tetrachlorodiborine was stirred at room temperature for 2 hours in the presence of excess diethyl ether. This statement is based on two observations. First, the amount of ether retained after evacuation of the mixture at -80° C. corresponded to an $\text{Et}_2\text{O}/\text{B}_2\text{Cl}_4$ ratio of only 1.64/1.00 instead of the 2/1 ratio characteristic of unchanged tetrachlorodiborine. In the second place, filtration of mixtures obtained by the interaction of ethereal solution of the tetrachloride with lithium hydride, showed the presence of an ether soluble solid containing active hydrogen. Too little of this material was obtained for analysis; whether it is lithium borohydride, or a compound such as $\text{Li}_2\text{B}_2\text{Cl}_4\text{H}_2$ only further study can disclose. All that can be said at present is that the reaction as carried out had probably not gone to completion, since the amount of active hydrogen in the ether soluble fraction was only about one-fifth of the hydrogen of the lithium hydride used. Repetition of the experiment is under way.

3.) The Reaction of Tetrachlorodiborine with Diborane.

An earlier study of the reaction of tetrachlorodiborine with diborane (F.R. '49, p. 5) gave results difficult to interpret because the reaction yielded only boron trichloride and unidentified viscous liquid and waxy solid materials, obtained in amounts too small for investigation.

The reaction has now been carried out in diethyl ether solution under which conditions the initial product seems to be a 1:1 adduct of B_2Cl_4 and B_2H_6 , i.e., possibly $B_4Cl_4H_6$. Thus, an ether solution containing 1.64 mmoles² of tetrachlorodiborane was allowed to stand in contact with 2.91 mmoles of diborane for 3 hours at room temperature. During this time the mixture turned yellow. (It has since been discovered that the discoloration can be avoided if the reaction is carried out at $-23^\circ C$.) From the solution, the excess of ether and of diborane was removed at $-80^\circ C$. Since the amount of unchanged diborane recovered was 1.31 mmoles, 1.68 mmoles had evidently been retained by the 1.64 mmoles of tetrachlorodiborane originally used. The residue having this one to one ratio is a slightly volatile, viscous liquid which undergoes slow decomposition at room temperature. Attempts to purify it by fractionation from room temperature ultimately led to the formation of a white, non-volatile solid and of volatile material consisting chiefly of ethyl chloride with smaller amounts of diborane and of ethane.

The present study indicates the formation of a 1:1 adduct of diborane and tetrachlorodiborane which is probably associated with ether in the solution in which it is formed. The observation that the formation of yellow by-products may be avoided by carrying out the initial reaction at $-23^\circ C$ may aid in the identification of the unstable liquid obtained when the ether is removed. Of particular interest, however, will be attempts to hydrogenate the adduct to ascertain whether dihydrotetraborane can be thus obtained.

4.) The Reaction of Tetrachlorodiborane with Ethylene.

A preliminary study of this reaction indicates the clean formation of a 1:1 adduct, which is a slightly volatile liquid having a 0° vapor tension of about 2 mm., and which appears to be homogeneous. The molecular weight of this material, determined by vapor density measurement, is also in agreement with a reaction ratio of 1:1. (M.W. found, 197; calculated for $B_2Cl_4 + C_2H_4$, 192.) Further studies are planned to ascertain whether the formation of the adduct involves a rupture of the boron to boron bond of the tetrachlorodiborane, followed by addition of BCl_2 fragments to the double bond in ethylene. At all events hydrogenation of the adduct might lead to interesting new types of boron-carbon compounds containing active hydrogen.

B. Reactions of Tetraboron tetrachloride, B_4Cl_4 .

1.) Reaction with Dimethyl Zinc.

The investigation of the behavior of tetraboron tetrachloride toward trimethyl boron and toward trimethyl aluminum, as reported in F.R. '52, p. 6, led to no clearcut results. The reaction with dimethyl zinc, on the other hand, appears to result in the formation of methyl derivatives, as is illustrated by the following experiment.

A mixture of 0.0375 g. (0.2027 mmole) and 0.4054 mmole of dimethyl zinc was allowed to stand for a half-hour at room temperature. A small amount of a red precipitate had formed, but most of the material consisted of a volatile liquid which was distilled at room temperature through traps maintained at -80° , -119° , and $-196^\circ C$. The last trap contained essentially pure trimethyl boron (-80° tension 32 mm). The fraction retained at $-119^\circ C$.

was not entirely pure, since its vapor tension, which originally was that of pure dimethyl zinc, slowly rose when the material was exposed to room temperature for several hours. Redistillation of this fraction through a -119°C . trap into one at -196°C . indicated that the rise was due to formation of additional trimethyl boron. This phenomenon was also observed with the product obtained by treating tetraboron tetrachloride with trimethyl aluminum.

The crystalline fraction retained at -80°C . had the appearance of unchanged tetraboron tetrachloride, but exhibited different vapor tensions as shown in Table XI.

Table XI

Vapor Tensions of B_4Cl_4 and of its Methylated Product

| | | | |
|---|-------|-------|-------|
| $t^{\circ}\text{C}$. | 46.10 | 50.10 | 55.40 |
| p_{mm} , CH_3 deriv. | 5.10 | 8.05 | 12.10 |
| p_{mm} , B_4Cl_4 | 7.00 | 11.25 | 15.38 |

The values in the second row may be satisfactorily reproduced by the equation

$$\log p_{\text{mm}} = \frac{-3282}{T} + 11.066$$

Those in the third row were calculated by the equation

$$\log p_{\text{mm}} = \frac{-2719}{T} + 9.464$$

(F.R. '52, p. 4).

That the product is probably a mono-methyl derivative of B_4Cl_4 is indicated by its vapor density and chlorine content. A sample weighing 0.0351 g. exerted a pressure of 17.45 mm. at 63.1°C . in a volume of 262 c.c.; these data correspond to a molecular weight of 162 as compared with the value 165 calculated for $\text{B}_4\text{Cl}_3(\text{CH}_3)$. The chlorine content of the sample was 62% as compared with the theoretical 64.6%. Use of a larger excess of dimethyl zinc in the preparative reaction did not appear to lead to further methylation. (It is, however, possible that the unstable material found associated with the excess dimethyl zinc in the -119°C . trap may have contained more highly methylated products which underwent spontaneous disproportionation.) Since these experiments were all carried out with very small amounts of starting material, they will be confirmed as soon as more of the tetraboron tetrachloride is available.

2.) Reaction of Tetraboron Tetrachloride with Methanol or Water.

The behavior of tetraboron tetrachloride toward water is similar to its reaction with methanol. In both reactions 6 g. equivalents of hydrogen are initially generated per mole of the tetrachloride, and 2 additional equivalents are liberated when a base is added. Hydrogen chloride

is formed by the hydrolysis, whereas methyl chloride is obtained by methanolysis. The similarity of the two reactions is brought out in Table XII, in which the symbol R represents either H or CH_3 .

Table XII

Molar Quantities of Reactants and Products per Mole of B_4Cl_4

| Molar Quantities | ROH required | Initial H_2 | H_2 alkal. Hydrol. | RC1 |
|------------------|--------------|----------------------|-----------------------------|------|
| Methanolysis | 5.99 | 3.06 | 0.982 | 3.96 |
| Hydrolysis | 5.75 | 2.98 | 1.01 | 3.92 |

Preliminary data for an unfinished experiment were reported in F.R. '52, p. 6. The experiment has now been completed as follows:

A 0.0450 g. (0.243 mmole) sample of tetraboron tetrachloride was treated with 32.60 (gaseous) c.c. or 1.455 mmole of methanol for 12 hours at room temperature. At the end of this period 16.7 c.c. (0.74 mmole) of hydrogen had been generated. There was also obtained 21.6 gaseous c.c. (0.964 mmole) of a material shown to be methyl chloride by its melting point of -97.5° (pure CH_3Cl has a recorded melting point of -97.7°C .) The white, non-volatile solid remaining in the reaction vessel generated an additional 5.25 c.c., or 0.234 mmole of hydrogen when treated with aqueous potassium hydroxide.

The use of a larger excess of methanol did not alter the amount of hydrogen obtained per mole of tetraboron tetrachloride. It did, however, complicate fractionation of the mixture. It was, nevertheless, possible to demonstrate qualitatively that methyl borate (in the form of its methanol azeotrope) is formed in addition to methyl chloride and hydrogen.

In the water reaction, 0.0233 g. (0.126 mmole) of tetraboron tetrachloride was treated with 16.25 c.c. (0.725 mmole) of water vapor. After 12 hours at room temperature, 8.42 c.c. (0.375 mmole) of hydrogen had been generated. The only other volatile product was 11.05 c.c. (0.494 mmole) of hydrogen chloride, identified by its vapor tension of 125 mm. at -112°C . The non-volatile solid generated 2.84 c.c. (0.127 mmole) of hydrogen when aqueous potassium hydroxide was added. All of these data have been summarized in the form of ratios in Table XII.

3.) Structure of Tetraboron Tetrachloride.

It was immediately recognized that the requirement of 6 moles of methanol or of water per mole of tetraboron tetrachloride and the accompanying generation of 6 g. equivalents of hydrogen could be best explained by a structure for B_4Cl_4 involving 6 equivalent boron to boron bonds. Such a structure would be represented by a regular (or slightly deformed) tetrahedron having at its corners boron atoms each of which is bound to a chlorine atom. This type of structure, which was also arrived at by W.N. Lipscomb

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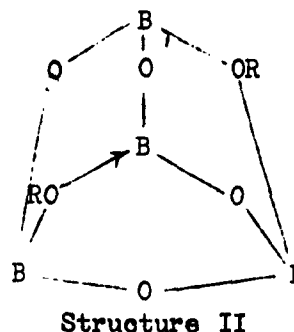
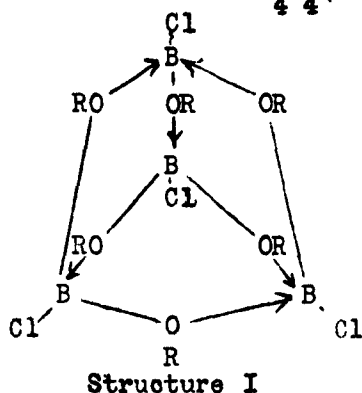
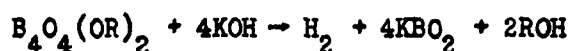
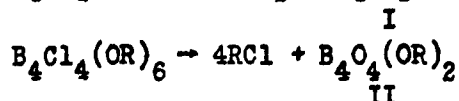
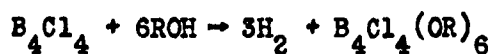
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(J. Chem. Phys., 21, 172 (1953) from x-ray studies of the crystals, has now received further support from the observation, reported in the previous section, that an additional 2 equivalents of hydrogen are generated when a base is added to the reaction mixture. Based on these observations a reasonable interpretation of the reactions involved as a first step the breaking of the boron to boron bonds and their conversion into boron-oxygen covalent and dative bonds as represented by the first of the following equations, and the suggested Structure I for the initial product (I).



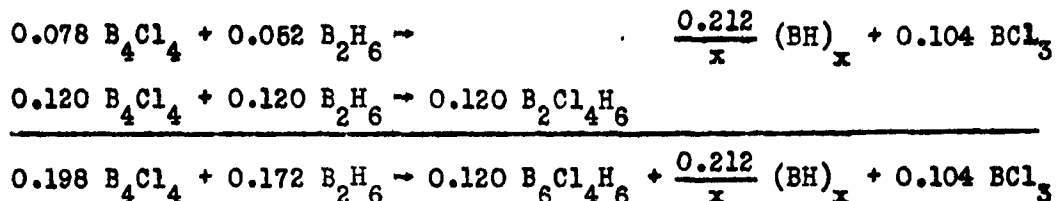
In these structural formulas, arrows indicate dative bonds. The second step (represented by the second equation) constitutes the loss of methyl chloride, and is analogous to the loss of ethyl chloride observed when the monoetherate of tetrachlorodiborane is warmed to room temperature. The product resulting from the liberation of methyl chloride is represented by Structure II, which visualizes a compound in which two boron atoms are in the state of complete oxidation and the remaining two atoms are in a less highly oxidized state. The last step in the reaction would then be represented by the third equation in which the conversion of the two boron atoms from the lower to the completely oxidized state accounts for the generation of two equivalents of hydrogen.

As soon as sufficient of the tetrachloride becomes available, the experiment is to be repeated with larger quantities of reactants in an attempt to isolate the assumed intermediate of Structure II.

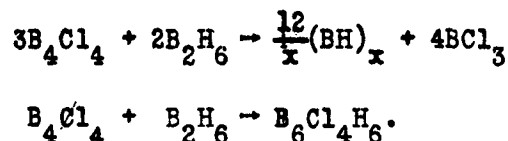
4.) The Reaction of Tetraboron Tetrachloride with Diborane.

A mixture of 0.0371 g. (0.200 mmole) of the subchloride and 8.88 c.c. of gaseous diborane (0.397 mmole) was heated in a sealed tube at 550° C. for 48 hours, by which time all of the tetrachloride had disappeared and the tube had become coated with a yellow solid. Fractionation of the volatile material yielded 2.32 c.c. (0.104 mmole) of boron trichloride, retained in a -126° C. trap, and 5.03 c.c. (0.225 mmole) of diborane condensed at -196° C. No other volatile material was obtained. Hence for 0.172 mmole of diborane consumed, 0.104 mmole of boron trichloride was produced.

In order to interpret these results, it may be tentatively assumed that the only product, other than boron trichloride, which accompanies the formation of the latter is a solid of the composition $(BH)_x$, a composition frequently characteristic of solids obtained by the decomposition of boranes. On the basis of this assumption it is possible to calculate the composition of the remaining non-volatile material from the data of the preceding paragraph, as illustrated by the following equations.



It will be seen that the prefixes of several individual components of the system have been so chosen that the quantities of diborane and tetraboron tetrachloride, as well as that of the boron chloride obtained, are those experimentally observed. To express these prefixes in whole numbers, the equations may be rewritten as follows:



Because of the small quantities used in the experiment, and because of the unproved assumption that there are only two solid products, one of which has the composition $(BH)_x$, these equations merely represent working hypotheses. They do suggest that a chlorine derivative of the little-known hexaborane (B_6H_{10}) may have been formed. This possibility is being explored further.

5.) Preparation of Tetraboron Tetrachloride.

It will have been observed that all of the preceding experiments on the reactions of tetraboron tetrachloride were carried out with extremely small quantities of starting material. During the course of the present contract year, a number of efforts have been made to find preparative methods which might give better yields of the tetrachloride than does the passage of boron chloride through a discharge between mercury electrodes. These efforts have involved a search for reducing agents, among which have been metal borides (prepared by the action of borohydrides on metal halides in aqueous and ethereal solutions). Since these experiments have not yet led to any improvement, they will not be reported further.

Apparatus in which boron trichloride may be automatically passed through 8 mercury arcs simultaneously and repeatedly has been constructed, and is producing quantities of tetrachlorodiborane adequate for laboratory studies, and larger amounts of tetraboron tetrachloride than hitherto available. Further work on these compounds should therefore be somewhat accelerated.

III. REACTIONS OF HYDRAZINES WITH DIBORANE AND RELATED COMPOUNDS.

In previous reports the reactions of hydrazine and of dimethyl hydrazine with diborane to form the adducts $N_2H_4 \cdot B_2H_6$ and $N_2H_2(CH_3)_2 \cdot B_2H_6$ and some of the properties of these compounds have been described (F.R. '51, pp. 5-7; F.R. '52, pp. 7-13). Similar adducts of hydrazine with trimethyl boron, and with tetramethyl diborane, i.e., $N_2H_4 \cdot 2B(CH_3)_3$ and $N_2H_4 \cdot B_2H_2(CH_3)_4$, have now been prepared and investigated, as described in the following sections of this report.

A. Preparation of the Adducts.

1.) General considerations.

The same procedures and precautions found necessary to obtain satisfactory results in the preparation of the adducts previously described (F.R. '51, p. 6) are necessary for the successful preparation of the adducts of hydrazine with trimethyl boron and with tetramethyl diborane, i.e., the hydrazine used must be of high purity, strictly air and moisture free conditions must be maintained, the reaction should be carried out at about $-80^\circ C.$, a solvent must be used, and the reaction mixture must be vigorously stirred for a long time. As in the previous experiments, diethyl ether proved a satisfactory solvent, but only if it is present in considerable excess are the best results obtained. The best procedure is to condense the trimethyl boron or the tetramethyl diborane into an ethereal solution of the hydrazine. Special details for each of the compounds under consideration are described in paragraphs (2) and (3).

2.) Preparation of the Compound $N_2H_4 \cdot 2B(CH_3)_3$.

Details of three preparative experiments are recorded in Table XIII.

Table XIII

Reaction of N_2H_4 with $B(CH_3)_3$

| Solvent | $t^\circ C.$ | Time Hours | Initial (mmoles) | | Recovered (mmoles) $B(CH_3)_3$ | Ratio $B(CH_3)_3/N_2H_4$ |
|---------|--------------|---------------|------------------|-------------|-----------------------------------|-----------------------------|
| | | | N_2H_4 | $B(CH_3)_3$ | | |
| Ether | 0 | 30 | 5.93 | 18.90 | 8.5 | 1.75 |
| Ether | -80 | 24 | 3.39 | 9.79 | 2.97 | 1.998 |
| None | -80 | 96 | 2.37 | 10.00 | 4.5 | 1.75 |

Only in the experiment in which the reaction mixture was maintained at $-80^\circ C.$ and in which the ether, used as solvent, was removed by evacuation at this temperature, was the expected ratio of trimethylboron to hydrazine obtained. The product was a solid which exerted a considerable vapor pressure at $0^\circ C.$ Examination of the vapor disclosed that it contained both ether and trimethylboron. It, therefore, seemed that the compound $N_2H_4 \cdot 2B(CH_3)_3$ dissociates at this temperature. It is obvious that, to measure the dissociation pressure of the compound, occluded ether has to be removed or avoided. No temperature was found at which all ether could be removed

without loss of trimethylboron and formation of some liquid hydrazine. On the other hand, preparation of the adduct in the absence of ether, at temperatures at which the adduct is completely stable, proved unsuccessful as shown in the third experiment of Table XIII. As a result no reliable value of the dissociation pressures has been obtained.

3.) Preparation of the Compound $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_2(\text{CH}_3)_4$.

The procedure for the preparation of the tetramethyldiborane-hydrazine adduct was like that for the trimethyl boron adduct, except that special precautions had to be taken to assure purity of the tetramethyldiborane, which disproportionates partially even at relatively low temperatures. The tetramethyldiborane was prepared by mixing diborane at room temperature with a large excess of trimethyl boron (6 - 10 moles per mole of B_2H_6). The mixture was then passed through a -80°C . trap into one at -196°C . The contents of the former were then warmed somewhat and again passed through the same train of traps; the procedure was repeated until the contents of the -80°C . trap had a 0° tension of 49 mm. A portion of the purified liquid was maintained at 0° in a vessel connected to a bulb of known volume. As soon as the pressure reached 48 mm., the bulb was disconnected from the vessel containing the liquid. The vapor, whose volume, temperature and pressure were thus known, was immediately condensed at -196° , and then passed through a -80° trap into one at -196° . The -80° condensate was then rapidly condensed into the reaction vessel, which contained a solution of hydrazine in ether at -196° . The portion of tetramethyldiborane which passed through the -80°C . trap was hydrolyzed to determine the amount of the compound lost during the process of its volume determination.

Experimental details are as follows. To a solution of 2.41 mmoles of hydrazine in about 15-20 ml. of diethyl ether, there were added 4.91 mmoles of tetramethyldiborane (0° tension, 48.5 mm.), measured out as described in the preceding paragraph. The mixture was warmed to -80°C ., and stirred for 26 hours. The ether and excess of tetramethyl diborane were then removed at -80°C . The quantity of the latter was determined (by hydrolysis and measurement of the hydrogen evolved) to be 2.50 mmoles. Hence, $4.91 - 2.50 = 2.41$ mmoles of tetramethyldiborane reacted with 2.41 mmoles of hydrazine.

The 1/1 adduct is a white solid which melts at about 10°C ., and seems not to dissociate at that temperature into the components from which it was formed. It is, however, difficult to ascertain whether dissociation occurs, because at room temperature decomposition accompanied by loss of hydrogen is observed, as is described in III,B, 2 of this report.

4.) Reaction of Hydrazine with Boron Trichloride.

In view of our previous experience, which showed that the reactions of hydrazine with several different boron compounds are difficult, if not impossible to carry to completion in the absence of solvents, the attempt to prepare a boron trichloride-hydrazine adduct was first made with ether as the solvent. Even at room temperature no, or only very slight interaction appeared to occur. It may, therefore, be concluded that the boron trichloride ethyl etherate is more stable toward dissociation into its components than is the (hypothetical) boron chloride-hydrazine adduct. In the absence of any liquid medium other than the two reactants, a strongly exothermic reaction results in the formation of a non-homogeneous solid which holds occluded hydrazine firmly. Further attempts to form the adduct in an inert solvent are contemplated.

B. Pyrolysis of the Compounds $N_2H_4 \cdot 2B(CH_3)_3$ and $N_2H_4 \cdot B_2H_2(CH_3)_4$.

1.) Pyrolysis of Mixtures of Hydrazine and Trimethyl Boron.

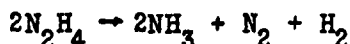
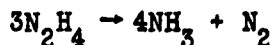
The objective of the study of hydrazine adducts with boron compounds is to ascertain whether by pyrolysis of such adducts polymeric substances of interest might be obtained, as is the case of boron adducts with ammonia and with amines. In view of the ease with which the compound $N_2H_4 \cdot 2B(CH_3)_3$ undergoes dissociation, the only possible approach to finding what products might be obtained by pyrolysis of the adduct, is to heat mixtures of hydrazine with large excesses of trimethyl boron, a reaction which was expected to result in the formation of methane as one of the reaction products. Since hydrazine is itself a metastable substance, several experiments were carried out to determine the lowest temperature at which methane is formed from the mixtures in question.

The mixtures used contained trimethyl boron and hydrazine in molar ratios of from 3/1 to 4/1. When they were heated to temperatures below 200° C. for as much as 4 hours, and were then cooled to room temperature, crystalline solids similar in appearance to the original $N_2H_4 \cdot 2B(CH_3)_3$ adduct were deposited, indicating that very little change had occurred. At temperatures above 200° C. or when heating at this temperature was continued over longer periods, condensation of the products at room temperature led to material differing markedly in appearance from that of the initial adduct, i.e., the material was a mixture of a liquid and a slightly volatile, amorphous solid. When the reaction vessel was opened, it was found to consist of material not completely condensable at -196° C in addition to several condensable products.

The latter were fractionated through traps at -80°, -112° and -196° C. The most volatile portion, condensed at -196° C., was almost pure trimethyl boron; the least volatile, retained at -80° C., was a liquid from which a slightly volatile solid slowly deposited. The major fraction, retained in the -112° C. trap, was a liquid which gradually went over to a cellophane-like solid at -80° C. At room temperature it evaporated slowly in vacuo, but could be recondensed from the vapor at -80° C. The density of the vapor, measured at 23° C. was found to correspond to a molecular weight of 56.4. All of these properties are in complete agreement with the properties of B-dimethylaminoborane, mol. wt. 56.8, as described by Schlesinger, Horvitz and Burg. (J. Am. Chem. Soc., 58, 409 (1936).)

For an understanding of the reaction it is necessary also to know the components of the non-condensable material, which could have contained hydrogen, methane and nitrogen. For analysis the non-condensable products were repeatedly circulated over cupric oxide wire maintained at 275-300° C., at which temperature hydrogen but not methane is oxidized. The contraction in volume which occurred on removal of the water formed was taken as a measure of the free hydrogen present in the initial gaseous reaction product. The remaining gas was recirculated over cupric oxide wire at from 800-900° C. to oxidize the methane. The carbon dioxide formed was condensed at -196° C., and then measured after revolatilization; the residual gas was considered to be nitrogen.

A conceivable interpretation of the observations is that the reaction occurs in steps: (1) the formation of ammonia by thermal decomposition of hydrazine, and (2) the interaction of ammonia with trimethylboron to produce B-dimethylaminoborane and methane. There is, however, a serious difficulty in accepting this interpretation, since pyrolysis of hydrazine usually occurs according to the equations:

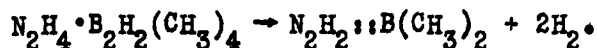


Although the relative extent to which each of these reactions occurs depends on the nature of the walls of the reaction vessel and on the presence of other catalytic material, it is unlikely that reaction should occur exclusively according to the first equation. Yet in the pyrolysis of hydrazine-trimethylboron mixtures no hydrogen was obtained. Whether this result is to be interpreted as meaning that removal of ammonia by trimethyl boron favors the first reaction to such an extent that it is practically the exclusive one, or whether the reaction is a direct one between hydrazine and trimethylboron cannot be decided until a complete material balance for the reaction has been obtained. Our present data are inadequate for this purpose and need amplification.

2.) Pyrolysis of the Compound $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_2(\text{CH}_3)_4$

The pyrolysis of mixtures of hydrazine with trimethylboron was undertaken in the expectation that the intermediate $\text{N}_2\text{H}_4 \cdot 2\text{B}(\text{CH}_3)_3$ would lose methane to form the product, $\text{N}_2\text{H}_4 \cdot 2\text{B}(\text{CH}_3)_2$. As pointed out in the preceding section, this reaction does not occur. The desired end result, namely the compound $\text{N}_2\text{H}_4 \cdot 2\text{B}(\text{CH}_3)_2$, should, however, be obtained by loss of hydrogen from the adduct $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_2(\text{CH}_3)_4$.

As already pointed out in section III, A, 3, of this report, the adduct in question actually begins to lose hydrogen at room temperature. Under continued pumping, the sample of the adduct obtained from 2.41 mmoles of hydrazine and 2.41 mmoles of tetramethyldiborane, lost 4.6 mmoles of hydrogen, i.e., very nearly the 4.82 mmoles expected according to the equation



In view of the small quantities involved, the agreement between the experiment and the equation is as good as could be expected.

The product resulting from the loss of hydrogen is a liquid, which was purified by fractionation in a train consisting of -80° and -196° C. traps. The material passing through the -80° trap proved to be ether which seems to be tenaciously held by the original adduct, as well as by its decomposition products. The -80° trap retained the liquid which is sufficiently volatile to permit the determination of its vapor density at 27.8° C. The value found corresponded to a molecular weight of 106.6, in contrast to the molecular weight of 111.6 calculated for the compound $\text{N}_2\text{H}_4 : 2\text{B}(\text{CH}_3)_2$. The discrepancy between the two values is ascribed to the presence of ether in the product used for the molecular weight determination, but the experimentally obtained value is strong support for the formula, as is the amount of hydrogen lost by the adduct.

The liquid decomposition product gradually deposits solid material which is presumably a polymer. It is soluble in benzene from which it can

C. Comparison of the Several Hydrazine Adducts and their Pyrolysis Products.

Although knowledge of the properties of the four hydrazine adducts thus far prepared is still rather fragmentary, it is of interest to compare them and their pyrolysis products briefly. All of the adducts are prepared by interaction of the components in ether solution at -80°C . All are crystalline solids of very low or no volatility. The adducts, $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_6$ and $\text{N}_2\text{H}_2(\text{CH}_3)_2 \cdot \text{B}_2\text{H}_6$ do not melt at temperatures below which loss of hydrogen sets in. The compound $\text{N}_2\text{H}_4 \cdot 2\text{B}(\text{CH}_3)_3$, heated under trimethyl boron pressure to prevent dissociation, seems to melt at about 50°C ., although the formation of liquid at this temperature may be due to partial dissociation; the adduct $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_2(\text{CH}_3)_4$ melts at about 10°C . The only one of the adducts which has been shown to dissociate into its components at temperatures below which more extensive decomposition occurs, is the trimethyl boron adduct.

It is assumed that these adducts are all borine derivatives, as are the adducts of ammonia with comparable boron compounds. In other words, it

is assumed that they have the formula: $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{R}_3\text{B} : \text{N} - \text{N} : \text{BR}_3 \end{array}$ in which R is either a hydrogen atom or a methyl group. (In the case of the diborane-dimethyl

hydrazine adduct, the formula is $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}_3\text{B} : \text{N} - \text{N} : \text{BH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$.) When they are heated

they lose hydrogen, or, in the case of the trimethyl boron-hydrogen adduct, methane. Except for the trimethyl boron adduct, this decomposition occurs without breaking of the nitrogen to nitrogen bond and presumably leads to the forma-

tion of compounds of the type $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{R}_2\text{B} \leftarrow \text{N} - \text{N} \rightarrow \text{BR}_2 \end{array}$, which are analogous to aminoborines, e.g., $\text{R}_2\text{B} \leftarrow \text{NH}_2$. Loss of hydrogen by the adduct $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_6$ occurs at 100° but does not become rapid till the temperature is raised to about $125-130^{\circ}\text{C}$.; in the case of the adduct $\text{N}_2\text{H}_2(\text{CH}_3)_2 \cdot \text{B}_2\text{H}_6$ hydrogen loss begins at 70°C . and becomes rapid above 750°C ., while for the adduct $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_2(\text{CH}_3)_4$ loss of hydrogen occurs at room temperature. In the case of the compound, $\text{N}_2\text{H}_4 \cdot 2\text{B}(\text{CH}_3)_3$, this type of hydrogen loss, i.e., a loss involving hydrogen atoms from both nitrogen and boron, cannot occur. The corresponding loss of methane requires a much higher temperature than the loss of hydrogen from hydrazine adducts, and is accompanied by breaking of the nitrogen to nitrogen bonds. The decomposition product, $\text{H}_3\text{B}(\text{NH})_2\text{BH}_3$, is a solid which loses hydrogen very slowly at the temperature at which it is formed from $\text{H}_3\text{B}(\text{NH})_2\text{BH}_3$. It is non-volatile and has not yet been purified since no solvent for it has been found. (It is insoluble in benzene or carbon tetrachloride, and only very slightly soluble in ether.) Both the decomposition products $\text{H}_3\text{B}(\text{N}-\text{CH}_3)_2\text{BH}_3$ and $\text{R}_2\text{B}(\text{NH})_2\text{BR}_2$ are moderately volatile liquids having vapor densities corresponding to the formulae mentioned. Both, however, seem to polymerize slowly to give solid substances which have not yet been studied further, as is true also of their further decomposition at higher temperatures.

IV. PYROLYSIS OF MIXTURES OF DIBORANE AND TRIMETHYL BORON.

C. Comparison of the Several Hydrazine Adducts and their Pyrolysis Products.

Although knowledge of the properties of the four hydrazine adducts thus far prepared is still rather fragmentary, it is of interest to compare them and their pyrolysis products briefly. All of the adducts are prepared by interaction of the components in ether solution at -80°C . All are crystalline solids of very low or no volatility. The adducts, $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_6$ and $\text{N}_2\text{H}_2(\text{CH}_3)_2 \cdot \text{B}_2\text{H}_6$ do not melt at temperatures below which loss of hydrogen sets in. The compound $\text{N}_2\text{H}_4 \cdot 2\text{B}(\text{CH}_3)_3$ heated under trimethyl boron pressure to prevent dissociation, seems to melt at about 50°C ., although the formation of liquid at this temperature may be due to partial dissociation; the adduct $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_2(\text{CH}_3)_4$ melts at about 10°C . The only one of the adducts which has been shown to dissociate into its components at temperatures below which more extensive decomposition occurs, is the trimethyl boron adduct.

It is assumed that these adducts are all borine derivatives, as are the adducts of ammonia with comparable boron compounds. In other words, it

is assumed that they have the formula: $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{R}_3\text{B} : \text{N} - \text{N} : \text{BR}_3 \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ in which R is either a hydrogen atom or a methyl group. (In the case of the diborane-dimethyl

hydrazine adduct, the formula is $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}_3\text{B} : \text{N} - \text{N} : \text{BH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$.) When they are heated

they lose hydrogen, or, in the case of the trimethyl boron-hydrogen adduct, methane. Except for the trimethyl boron adduct, this decomposition occurs without breaking of the nitrogen to nitrogen bond and presumably leads to the forma-

tion of compounds of the type $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{R}_2\text{B} = \text{N} - \text{N} = \text{BR}_2 \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$, which are analogous to aminoborines, e.g., $\text{R}_2\text{B} = \text{NH}_2$. Loss of hydrogen by the adduct $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_6$ occurs at 100° but does not become rapid till the temperature is raised to about $125-130^{\circ}\text{C}$.; in the case of the adduct $\text{N}_2\text{H}_2(\text{CH}_3)_2 \cdot \text{B}_2\text{H}_6$ hydrogen loss begins at 70°C . and becomes rapid above 750°C ., while for the adduct $\text{N}_2\text{H}_4 \cdot \text{B}_2\text{H}_2(\text{CH}_3)_4$ loss of hydrogen occurs at room temperature. In the case of the compound, $\text{N}_2\text{H}_4 \cdot 2\text{B}(\text{CH}_3)_3$ this type of hydrogen loss, i.e., a loss involving hydrogen atoms from both nitrogen and boron, cannot occur.

The corresponding loss of methane requires a much higher temperature than the loss of hydrogen from hydrazine adducts, and is accompanied by breaking of the nitrogen to nitrogen bonds. The decomposition product, $\text{H}_3\text{B}(\text{NH})_2\text{BH}_3$, is a solid which loses hydrogen very slowly at the temperature at which it is formed from $\text{H}_3\text{B}(\text{NH})_2\text{BH}_3$. It is non-volatile and has not yet been purified since no solvent for it has been found. (It is insoluble in benzene or carbon tetrachloride, and only very slightly soluble in ether.) Both the decomposition products $\text{H}_3\text{B}(\text{N}-\text{CH}_3)_2\text{BH}_3$ and $\text{R}_2\text{B}(\text{NH})_2\text{BR}_2$ are moderately volatile liquids having vapor densities corresponding to the formulae mentioned. Both, however, seem to polymerize slowly to give solid substances which have not yet been studied further, as is true also of their further decomposition at higher temperatures.

IV. PYROLYSIS OF MIXTURES OF DIBORANE AND TRIMETHYL BORON.

It was thought for several reasons the pyrolysis of methyl diboranes might lead to results worthy of study. The difficulty of preparing these compounds and their marked tendency to disproportionate into each other, as well as into trimethylboron and diborane, made it advisable to carry out the

investigation by pyrolysing mixtures of diborane and trimethylboron, since such mixtures contain the methyldiboranes.

As mentioned in the introductory section of this report, the results of such pyrolyses are bound to be complex, and thus far only exploratory experiments have been carried out to ascertain whether the results of more detailed study will warrant the effort they will require. Thus far no experiments involving circulatory systems have been carried out -- the four that have been made consisted of heating the samples in one-liter bulbs to about 150°. Some of the observations resulting from these experiments are recorded in Table XIV. In column 7, the symbols have the following meanings: + = slight amount, ++ = moderate amount, +++ = relatively large amount, w = white, and y = yellow.

Table XIV
Effects of Pyrolysis of $B(CH_3)_3 \cdot B_2H_6$ Mixtures
at 150° C. in One Liter Sealed Bulbs

| 1 Expt. | 2 B_2H_6 (cc) | 3 $\frac{B(CH_3)_3}{B_2H_6}$ | 4 Time hours | 5 H_2 (cc) formed | 6 B_2H_6 (cc) recovered | 7 Solids | 8 H_2/B_2H_6 per hr. |
|------------|-----------------------|---------------------------------|--------------------|---------------------------|---------------------------------|---------------|------------------------------|
| 1 | 181.5 | 0 | 1.5 | 195.3 | 33.6 | {+++ w, y. | 0.72 |
| 2 | 151.0* | 0.76 | 1.75 | 156.6 | 0.0 | {++ w, y. | 0.78* |
| 3 | 158.7 | 1.95 | 1.75 | 50.2 | trace | + , w. | 0.18 |
| 4 | 37.4 | 6.35 | 12.0 | 33.6 | 0.0 | almost 0 | 0.07 |

* This experiment is not entirely comparable to the others since the temperature rose to 170° C. during the heating.

Only in experiment 1 was the formation of any decaborane observed.

Two points brought out in the table are particularly noteworthy: (1) that, although the heating time was the shortest, the amount of solid formed was by far the greatest and its character the least uniform in the experiment in which diborane was heated by itself; and (2) that in this experiment over 35% of the total hydrogen present in the original diborane was generated as free hydrogen. In experiment 3 only about 10% of the hydrogen was so generated and much less solid was formed. The amount of hydrogen generated in 1.5-1.75 hours in experiment 4, in which the relative amount of trimethylboron was the largest, was extremely small; 12 hours instead of 1.5 hours were required to generate 30% of the total hydrogen, and there was only a barely noticeable amount of solid. Experiment 2 is not included in this discussion because of the fact that the temperature rose inadvertently above 150° C. during the heating period. (The absence of diborane in the products, except in experiment 1, is probably of no great significance, since it may all have been present in the other experiments as one or the other of its methyl derivatives.)

It is as yet impossible to interpret these results since it must first be established whether the effect of trimethylboron on the course of pyrolysis is a specific one, or whether it could be reproduced by the presence

of an inert gas, e.g., nitrogen. In the second place, it is as yet impossible to decide whether the observed effects are the result of a decrease in the rate of decomposition or whether they result from a change in the stoichiometry of the reaction. The latter possibility is suggested by the fact that in the presence of trimethylboron there are obtained smaller amounts of solids whose formation would be attended by the evolution of the larger quantities of hydrogen.

It should also be mentioned that in the experiments in which trimethylboron was present, liquid products were always obtained. So far as present indications go, they seemed to contain methylated boranes. Their identification may prove difficult since the more highly methylated diboranes have vapor tensions approaching those of pentaborane.

We are of the opinion that further study of the pyrolysis of diborane in the presence of trimethylboron (or of inert gas) should be undertaken. The marked decrease in the amount of solids formed at 150° - 175° may mean that higher temperatures, (which would diminish the likelihood of the formation of dihydropentaborane (B_5H_{11})) may be employed without corresponding loss of volatile boranes. This supposition receives some support from the fact that none of the reaction products obtained in the presence of trimethylboron spontaneously lost hydrogen at room temperature, as would have been the case had dihydropentaborane been present.

Unfortunately, Dr. Steindler, who carried out the experiments herein reported, has left the project. How soon a replacement will be ready to undertake the difficult work cannot yet be predicted. He has prepared tables of infra-red data which should be of value in identifying the products obtained in future work.

V. OTHER EXPERIMENTAL WORK UNDERTAKEN DURING THE PRESENT CONTRACT YEAR.

A. The Preparation of B-methyl, B-chloroborazoles.

The reasons for desiring to prepare B-dimethyl, B-monochloroborazole have been stated in the introduction. The procedure studied is the replacement of chlorine atoms in trichloroborazole by methyl groups. Grignard reagents requiring the use of ether were avoided because of the complications the presence of the latter might cause. Trimethylboron and dimethyl zinc in the absence of solvents were ineffective as methylating agents, but dimethyl zinc in toluene solution at about 50° C. seemed promising. Further work is in progress.

B. Some Additional Experiments on the Reduction of Tetrachlorodiborine by borides to form tetraboron tetrachloride have so far given only negative results.

C. A few experiments on the use of iodine as a catalyst in the formation of sodium aluminum hydride were assigned to one of the inexperienced new assistants to give him experience in hydride work. No improvements over older methods were achieved.

VI. PUBLICATIONS DURING THE PRESENT CONTRACT YEAR.

The following papers have been published during the present contract year and have been sent to the distribution list for the project. The series of papers entitled "New Developments in the Chemistry of Diborane and the Borohydrides" contains much subject matter resulting from projects carried out under the auspices of the National Research Committee, the Office of Scientific Research and Development and the Signal Corps Ground Signal Agency, in addition to the work done under Navy auspices. The organization of the work and the writing of the papers, however, occupied a considerable amount of time of the director of the present project, and are therefore included herein.

A New Sub-Chloride of Boron, B_2Cl_4 , by Grant Urry, Thomas Wartik and H.I. Schlesinger, J. Am. Chem. Soc., 74, 5809 (1952).

New Developments in the Chemistry of Diborane and the Borohydrides.

- I. General Summary, by H.I. Schlesinger, Herbert C. Brown, et al., J. Am. Chem. Soc. 75, 186 (1953).
- II. Improved Arc Process for the Preparation of Diborane, Purification of Diborane, by H.I. Schlesinger, Herbert C. Brown, B. Abraham, Norman Davidson, A.E. Finholt, R.A. Lad, J. Knight, and Anthony M. Schwartz, *ibid.*, 191.
- III. Addition Compounds of Alkali Metal Hydrides. Sodium Trimethoxyborohydride and Related Compounds, by Herbert C. Brown, H.I. Schlesinger, Irving Sheft and D.M. Ritter, *ibid.*, 192.
- IV. Reaction of the Boron Halides with the Alkali Metal Hydrides and with their Addition Compounds; A New Synthesis of Diborane, by H.I. Schlesinger, Herbert C. Brown, James R. Gilbreath and J.J. Katz, *ibid.*, 195.
- V. Reactions of Diborane with Alkali Metal Hydrides and their Addition Compounds. New Syntheses of Borohydrides. Sodium and Potassium Borohydrides, by H.I. Schlesinger, Herbert C. Brown, Henry R. Hoekstra and Louis R. Rapp, *ibid.*, 199.
- VI. The Preparation of Sodium Borohydride by the High Temperature Reaction of Sodium Hydride with Borate Esters, by H.I. Schlesinger, Herbert C. Brown and A.E. Finholt, *ibid.*, 205.
- VII. The Preparation of Other Borohydrides by Metathetical Reactions Utilizing the Alkali Metal Borohydrides, by H.I. Schlesinger, Herbert C. Brown and Earl K. Hyde, *ibid.*, 209.
- VIII. Procedures for the Preparation of Methyl Borate, by H.I. Schlesinger, Herbert C. Brown, Darwin L. Mayfield and James R. Gilbreath, *ibid.*, 213.
- IX. Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen, by H. I. Schlesinger, Herbert C. Brown, A.E. Finholt, James R. Gilbreath, Henry R. Hoekstra and Earl K. Hyde, *ibid.*, 215.
- X. Uranium (IV) Borohydride, by H.I. Schlesinger and Herbert C. Brown, *ibid.*, 219.
- XI. The Methyl Derivatives of Uranium (IV) Borohydride, by H.I. Schlesinger, Herbert C. Brown, L. Horvitz, A.C. Bond, L.D. Tuck and A.O. Walker, *ibid.*, 222.

Reactions of Hydrazine and of Symmetrical Dimethyl Hydrazine with Diborane,
by M. J. Steindler and H.I. Schlesinger, ibid., 756.

Reactions of Lithium Aluminum Hydride with Alkyls of Representative Elements
of the Main Groups of the Periodic System, by Thomas Wartik and H.I.
Schlesinger, ibid., 835.